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Thermal Processing and Composite Laminate Formation of Ionic Block Copolymers for Protective Clothing

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Thermal Processing and Composite Laminate Formation of Ionic Block Copolymers for Protective Clothing

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1. Introduction

The development of "breathable" protective clothing is a main goal in outfitting the future U.S. Army soldier. Currently, butyl rubber is one of the standard materials used for chemical protective clothing (CPC). Butyl rubber provides a sufficient barrier to chemical agents, but it is also a barrier to water vapor, which results in unbearable levels of heat stress on the soldier [1]. Future materials design should focus on the development of highly selective CPC (i.e., an excellent chemical agent barrier, but also breathable and comfortable). Additionally, future CPC materials need to be lightweight, flexible, and durable to withstand battlefield conditions. Incorporating all of these properties into one material is a great technical challenge.

Recently, investigators at the U.S. Army Research Laboratory (ARL) have developed a new material, an ionic block copolymer—highly sulfonated poly(styrene-isobutylene-styrene) (S-SIBS)—that possesses many of the desired properties for CPC [2]. S-SIBS contains two components: a flexible elastic barrier component and a hydrophilic breathable component. This new material is designed at a molecular level and self-assembles into unique structures on a nano level. Combining these different properties together into distinct nanostructures provides an excellent selective barrier for this application.

In order to incorporate S-SIBS into a future garment, research will be required in a number of areas, particularly polymer processing. This study demonstrates a first attempt in processing S-SIBS into thin films (without the use of toxic solvents) and laminating it into a polymer/fabric composite for use as CPC.

2. Experimental

2.1 Materials

Synthesis of S-SIBS was conducted at ARL, and the details of this procedure are documented elsewhere [2]. A standard battle dress uniform (BDU) fabric (50%/50% cotton/nylon), provided by the Natick Soldier Center (NSC), was used to produce polymer/fabric composites. Shore A 40, 50, and 55 firmness rubber sheets, Teflon* fluoropolymer sheets, and 0.64-cm (1/4-in) thick aluminum plates were used in the thermal processing procedure.

2.2 Equipment

A liquid nitrogen-cooled freezer mill (Spex CertiPrep 6750-115) was used to cryogenically grind the polymer. For thermal processing, a computer-controlled heat press (Tetrahedron Inc. MTP-

* Teflon is a registered trademark of E.I. du Pont de Nemours and Company.

24) was used. Infrared spectra of all polymer samples were collected using a Nicolet Nexus 870 Spectrometer equipped with a diamond ATR objective (Spectra-Tech Infinity Series). The diamond ATR objective (refractive index = 2.73) is a nondestructive technique that provides intimate contact with the polymer sample. Infrared spectra were collected using 500 scans and a 4 cm^{-1} resolution.

2.3 Polymer Preparation

2.3.1 Cryogenic Grinding

Two grams of S-SIBS were cut into small (5 × 5 mm) pieces and placed into the steel-grinding cartridge of the freezer mill. The mill was cooled with liquid nitrogen for 25 min before grinding. The polymer was then ground in 6 cycles of 4 min each with 4-min rest intervals (power setting = 10). The ground powder was then placed in a specimen jar to keep out moisture. The powder was dried in a vacuum oven at 40 °C for 2 hr and then placed in a desiccant container overnight to limit moisture uptake. Figure 1 shows an example of the polymer powder produced using this procedure.

Figure 1. Cryogenically ground polymer powder.

2.3.2 Heat Press Preparation

To prepare the heat press for thermal processing, aluminum caul plates, with dimensions of 30.48 × 30.48 × 0.64 cm (12 × 12 × 1/4 in), were used with at least one face machined and polished to a 0.0032-μm (0.125-μin) finish. The polymer powder was sandwiched between the caul plates, rubber, and Teflon sheets. As shown in Figure 2, the order of rubber and Teflon layers was from softest to hardest. The first caul plate was covered with a Teflon sheet, 0.16 cm

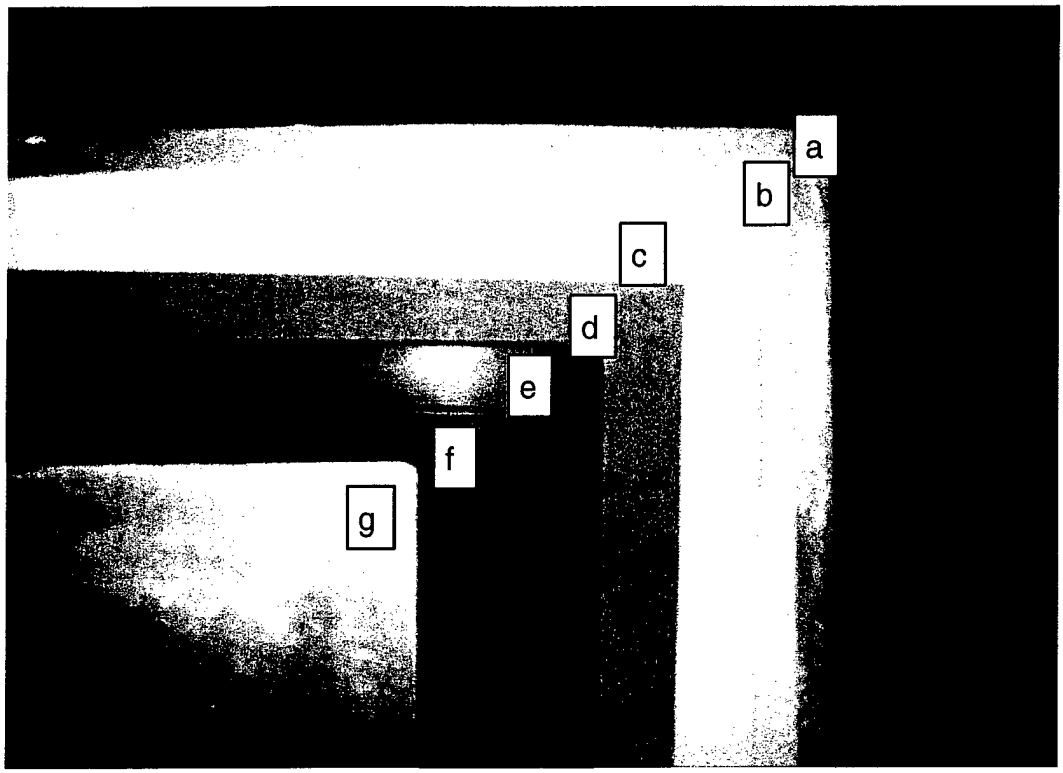

Figure 2. Heat press assembly: (a) caul plate, (b) Teflon sheet, (c) Teflon sheet, (d) 40 Shore A (tan) 1/16 in, (e) 50 Shore A (black) 1/16 in, (f) 55 Shore A (black) 1/4 in, and (g) caul plate.

(1/16 in) thick, followed by the polymer powder and a second Teflon sheet. Three layers of rubber sheets were used. The first (Shore A 40) and second (Shore A 50) rubber sheet were 30.48 × 30.48 × 0.16 cm (12 × 12 × 1/16 in) in size. The third rubber layer was 0.64 cm (1/4 in) thick and was slightly larger than the desired final dimensions of the polymer film (i.e., 15.24 × 15.24 cm or 6 × 6 in).

The polymer powder was processed using several programmable steps identified as programs 1–3 (Appendix A, Tables A-1 through A-3). The configuration shown in Figure 2 was used for program 1 only. A second set of caul plates, coated with Frekote* for a release film, was used for programs 2 and 3.

2.4 Thermal Pressing Procedure

A specified amount of S-SIBS powder was distributed over the Teflon sheet with a razor blade to a dimension slightly larger than the desired dimension of the polymer film. Experimentation revealed that 1 g of polymer powder can cover ~38.71 cm^2 (6 in^2). The second Teflon sheet and layers of rubber were placed on top of the polymer powder, and program 1 (Appendix A, Table A-1) was used to convert most of the polymer powder to a film with an initial melt process. To

* Frekote is a registered trademark of Loctite Corporation.

convert the remaining powder to a film form, program 2 (Appendix A, Table A-2) was used to produce the final product (freestanding film) by an increase of pressure at the same temperature.

2.5 Laminating Procedure

Program 3 (Appendix A, Table A-3) was used to laminate processed polymer films onto the BDU fabric, where both fabric and film were pressed together between two caul plates and a Teflon sheet. Further instructions are listed in Appendix B.

3. Results and Discussion

3.1 Pressed Polymer Film

Figure 3 shows a freestanding film created using programs 1 and 2. Initially, films produced with program 1 were not uniform in thickness and contained areas that were not completely converted from powder to film. The increase in pressure in program 2 produces complete films with uniform thicknesses ranging from 254 to 300 μm (10–13 mils) from film to film. The films produced weighed ~327.9 g/m^2 (9.7 oz/yd^2) in accordance with American Society for Testing and Materials (ASTM) standard D3776-96 [3]. The films were translucent, containing a brownish tint. The color is related to the amount of ionic groups (sulfonic acid) in the polymer. Higher ion contents usually correspond to darker shades of brown (shown in Figure 4). Pressing the polymer powder without the use of rubber sheets when using program 1 produces a poor film (e.g., Figure 5). The Teflon/rubber layers act as an insulator from the heated caul plates and allows convection heating over conductive. This process results in a more uniform film thickness. Different rubber layers provide an evenly distributed load transfer from the caul plates to the polymer powder during heating and pressure.

3.2 Laminated Polymer/Fabric Composite

Figures 6 and 7 show a laminated polymer/fabric composite (top/outer, bottom/inner, and side view) produced using program 3. The BDU fabric used here was ~356 μm (14 mils) and weighed 168.2 g/m^2 (5.0 oz/yd^2) in accordance with ASTM D3776-96. This makes the total weight of the polymer/fabric composite ~500 g/m^2, which increases the weight of the BDU fabric threefold.

3.3 Infrared Analysis

The infrared spectra of both solvent-cast and pressed films were examined to determine if any chemical changes occurred in the polymer due to heat pressing (shown in Figure 8). The four peaks, 1155, 1125, 1034, and 1007 cm^{-1}, are all infrared stretching vibrations associated with the ionic functional group in S-SIBS. Figure 8 shows that there is a negligible difference between the two spectra confirming that there is no chemical change in the polymer due to heat pressing the polymer.

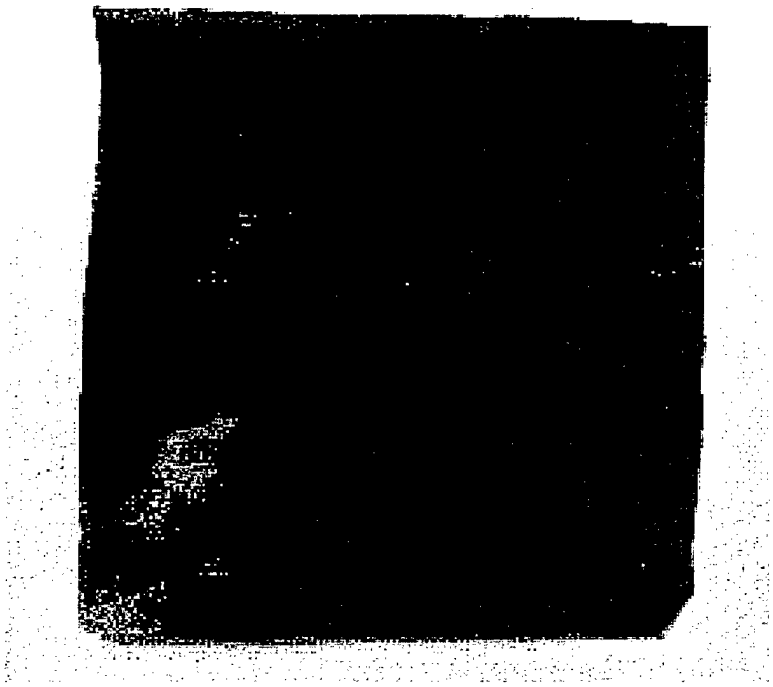

Figure 3. Pressed polymer film.

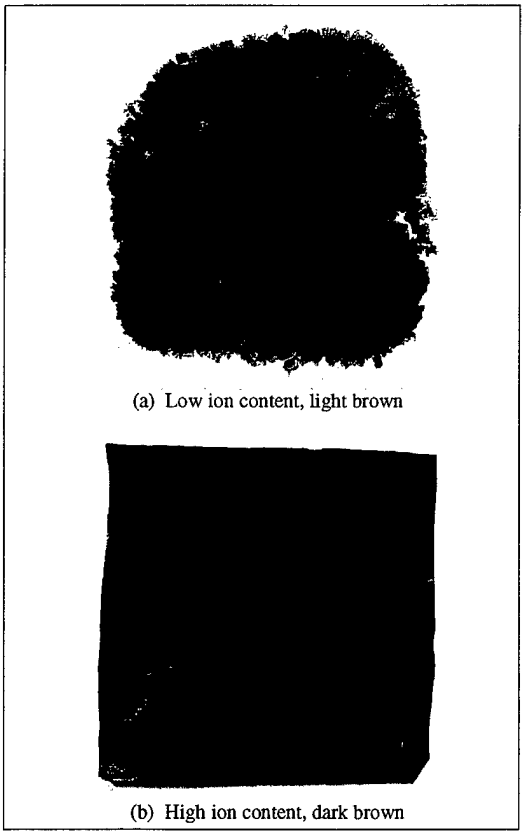

Figure 4. Pressed polymer films of (a) low and (b) high ion content.

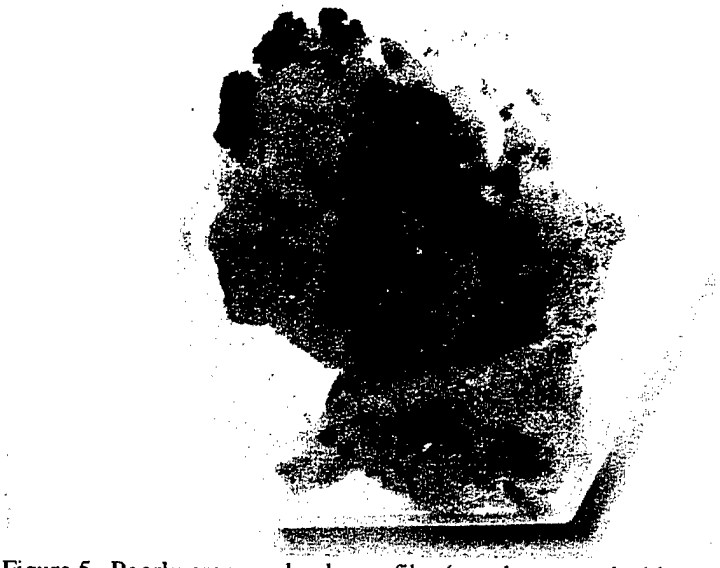

Figure 5. Poorly processed polymer film (powder pressed without using rubber sheets in heat press).

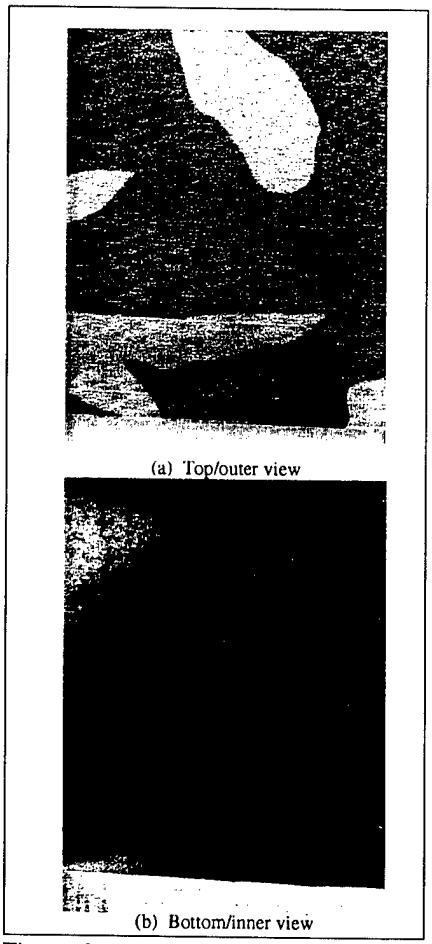

Figure 6. Polymer/fabric composite, (a) top and (b) bottom views.

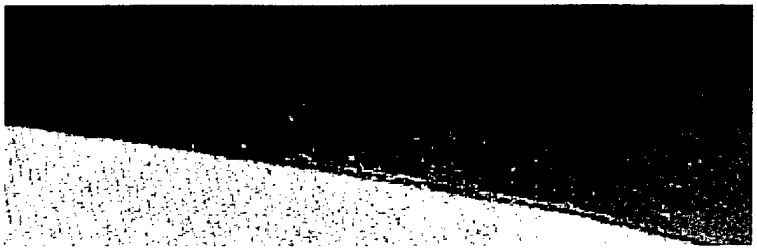

Figure 7. Polymer/fabric composite (side view).

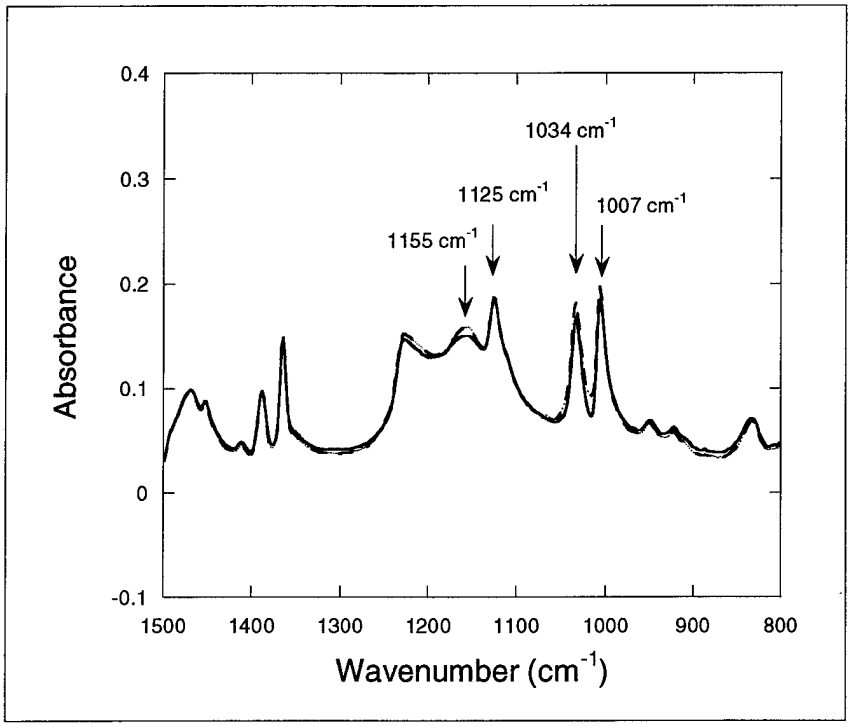

Figure 8. Infrared spectrum of solvent-cast (solid line) and pressed (dashed line) films.

4. Conclusion

In this study, a new material, previously developed by researchers at ARL, was thermally pressed into a thin film and laminated onto a BDU fabric. This investigation demonstrates the ability to produce polymer/fabric composites using an environmentally friendly process (without the use of toxic solvents) that can easily be scaled-up to a larger production. This work addresses the need for the future development of CPC as an everyday lightweight garment opposed to current bulky protective overgarments.

Future studies will be required to address several shortcomings in this study, such as reducing film thickness (for reducing weight), increasing adhesive strength between polymer and fabric, and developing practical procedures for scaling up this process. In addition, future experiments will need to be conducted to determine the durability (mechanical testing) and selectivity (transport testing) of the new polymer/fabric composite.

5. References

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2. Napadensky, E., Y. A. Elabd, J. M. Sloan, and D. M. Crawford. U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, unpublished data.
3. American Society for Testing and Materials. "Standard Test Methods for Mass per Unit Area (Weight) of Fabric." ASTM D3776-96, West Conshohocken, PA, 1996.

Appendix A. Programmable Steps

Table A-1. Program 1.

Step	Temperature		Temperature Rate		Force		Force Rate		Dwell Time	Go to Step
	(°C)	(°F)	(°C/min)	(°F/min)	(N)	(kips)	(N/min)	(kips/min)	(min)	
1	107	225	13.91	25	4450	1	4450	1	5	1.2
2	107	225	13.91	25	20000	4.5	20050	4.5	15	1.3
3	37.8	100	13.91	25	20000	4.5	20050	4.5	2	1.4
4	OFF	OFF	—	—	—	—	—	—	—	—

Table A-2. Program 2.

Step	Temperature		Temperature Rate		Force		Force Rate		Dwell Time	Go to Step
	(°C)	(°F)	(°C/min)	(°F/min)	(N)	(kips)	(N/min)	(kips/min)	(min)	
1	107	225	13.91	25	22200	5	22200	5	2	2.2
2	107	225	13.91	25	267000	60	88900	20	15	2.3
3	37.8	100	13.91	25	22200	5	88900	20	2	2.4
4	OFF	OFF	—	—	—	—	—	—	—	—

Table A-3. Program 3.

Step	Temperature		Temperature Rate		Force		Force Rate		Dwell Time	Go to Step
	(°C)	(°F)	(°C/min)	(°F/min)	(N)	(kips)	(N/min)	(kips/min)	(min)	
1	48.9	120	5.6	10	267000	60	88900	20	20	3.2
2	26.7	80	11.3	20	44500	10	88900	20	2	3.3
3	—	OFF	—	—	—	—	—	—	—	—

Appendix B. Further Instructions

- If any defects to films were found after visual inspection, additional powder was placed over defective areas and program 2 was repeated. This process can be repeated several times to ensure defect-free films.
- Pressing the powder using program 1 with only the Teflon* fluoropolymer sheet and caul plates will not work well. Pressing the powder without the rubber sandwich did not produce a workable film. However, it is possible to make one using repetitions of program 2. Films produced this way will be much thicker than normal.
- Use one sheet of Teflon whenever programs 2 and 3 are being run to improve the surface quality of the film. This will also help to prevent cracks and holes from occurring.
- Do not press the fabric and film together in the rubber sandwich. This will destroy the fabric, the film, and the Teflon sheets.
- Take care to ensure that the cylinders on the cryogenic grinder are tightly put together or powder will escape and be ruined.
- Be patient spreading the powder. It needs to be as evenly distributed and uniform as possible. Take your time.
- Use the razor blade to lift the edges of the film off the Teflon or caul plate before attempting to remove the film altogether. This will help to reduce the risk of tearing the film.
- As stated in section 3 of this report, the film can be repaired using either powder or film as a patch. This will cause the film to spread out at the higher pressures at program 2 and may cause cracking. Use one Teflon sheet to help prevent cracking.
- Pressure seems to be more important than temperature in this process.
- A new application of 3–5 coats of Frekote† releasing agent is needed for approximately every three repetitions.
- In general, this process works extremely well. However, it produces highly variable results in the time to complete a single film. On average, it takes 1 day to make and laminate two films.
- Learning how to make the films, at this point, and being proficient is all trial and error.

* Teflon is a registered trademark of E.I. du Pont de Nemours and Company.

† Frekote is a registered trademark of Loctite Corporation.

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14. ABSTRACT

The future U.S. Army soldier will require lightweight, flexible, durable, and selectively protective clothing for the battlefield. Current chemical protective clothing is worn as an overgarment and is impermeable to moisture vapor, imposing unbearable amounts of heat stress on the soldier. A new material, an ionic block copolymer, developed by researchers at the U.S. Army Research Laboratory, is both flexible and a "breathable" protective barrier. This study focuses on thermally processing and laminating this new material onto the standard battle dress uniform (BDU).

Polymer films were produced by cryogenically grinding the polymer to a powder and then thermally pressing it into a film. Films were pressed at 1.15 × 107 Pa (1668 psi) and 100 °C and were uniform in thickness, with thicknesses ranging from 254 to 300 μm (10–13 mils) from film to film. Films were then laminated onto a standard cotton/nylon BDU fabric using a similar pressure, but lower temperature (50 °C). The polymer/fabric composite nearly doubled the thickness of the fabric and increased the weight threefold. Additionally, infrared spectroscopy revealed no chemical change occurred in the pressed polymer films due to thermal processing.

15. SUBJECT TERMS
polymer processing, laminate formation, protective clothing, ionic block copolymer

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